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LETTER

Delayed microstructural recovery in silver processed by equal-channel angular pressing

Jenő Gubicza · Nguyen Q. Chinh · János L. Lábár · Zoltán Hegedűs · Péter Szommer · Géza Tichy · Terence G. Langdon

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Introduction

It is well known that above a certain grain size limit ($\sim$20 nm) the strength of materials increases with decreasing grain size [1, 2]. This feature has initiated a considerable current interest in the production and properties of ultrafine-grained (UFG) materials. The most attractive method for producing UFG metals in bulk form is through the application of severe plastic deformation (SPD) [3, 4] using procedures such as equal-channel angular pressing (ECAP) [5]. It has been shown for different pure face-centered cubic (fcc) metals processed by ECAP that the dislocation density increases while the grain size decreases with increasing strain and ultimately these parameters reach saturation values [6]. Recently, it was shown that processing by ECAP leads to an extremely high saturation dislocation density in pure silver ($\sim 46 \pm 5 \times 10^{14}$ m^{-2}) compared to other pure fcc metals (see Table 1 in [7]). It was suggested that this very high concentration of dislocations is due to the effect of the high degree of dislocation dissociation in silver which effectively hinders the ability for dislocation annihilation. In this report, the stability of this heavily deformed microstructure in silver is studied during storage at the same temperature used for the ECAP processing.

A high-purity 99.99% Ag billet having a length of $\sim$70 mm and a diameter of $\sim$10 mm was homogenized for 60 min at a temperature of 741 K (corresponding to 0.6 T_m, where T_m is the absolute melting point of Ag). It was then pressed through 8 passes in ECAP at room temperature using a pressing velocity of 8 mm s^{-1} and a die with an internal channel angle of 90°. The pressing was conducted using route B_c in which the billet is rotated about its longitudinal axis by 90° in the same direction after each pass [5]. For this die configuration, 1 pass corresponds to an equivalent strain of $\sim$1 [8]. It was shown recently that immediately following ECAP there is a relatively homogeneous grain structure in the material with an average grain size of $\sim$250 nm [7].

Following ECAP, the sample was stored in air at room temperature in order to study the stability of the internal microstructure. Microstructural evolution was examined as a function of the time of storage using X-ray line profile analysis on transverse sections lying perpendicular to the axes of the billets. Measurements of the X-ray diffraction lines were performed using a special high-resolution diffractometer (Nonius FR591) with CuKα_1 radiation (λ = 0.15406 nm). The line profiles were evaluated using the extended Convolutional Multiple Whole Profile (eCMWP) fitting procedure [9]. The microstructure immediately after ECAP and after 4 months of storage was also studied using a Philips CM-20 transmission electron microscope (TEM) operating at 200 kV.

Dedicated to Professor Tamás Ungár on the occasion of his 65th birthday.

J. Gubicza (✉) · N. Q. Chinh · J. L. Lábár · Z. Hegedűs · P. Szommer · G. Tichy
Department of Materials Physics, Eötvös Loránd University, Pázmány Péter s. 1/A., 1117 Budapest, Hungary
e-mail: gubicza@metal.elte.hu

N. Q. Chinh · T. G. Langdon
Departments of Aerospace & Mechanical Engineering and Materials Science, University of Southern California, Los Angeles, CA 90089-1453, USA

J. L. Lábár
Research Institute for Technical Physics and Materials Science, P.O. Box 49, 1525 Budapest, Hungary

T. G. Langdon
Materials Research Group, School of Engineering Sciences, University of Southampton, Southampton SO17 1BJ, UK

The hardness was determined as a function of the time of storage at room temperature for a period of up to 4 months. The hardness measurements were conducted using a Vickers microhardness indenter in a Shimadzu 202 machine with an applied load of 2000 mN. The deformation behavior was also studied before and after ECAP as well as after 4 months of storage using uniaxial compression testing with a computer-controlled hydraulic mechanical testing MTS 810 machine. The direction of compression was parallel to the longitudinal axis of each billet. The local mechanical behavior was examined by taking nanohardness measurements using a UMIS nanoindentation device with a Berkovich indenter and applying a maximum load of 5 mN. A series of 400 indentations was recorded with the indents arranged in a 20 × 20 matrix with the distance of 20 μm between neighboring indents.

Figure 1a shows the microhardness of silver processed by 8 ECAP passes as a function of time of storage at room temperature. It is apparent that the hardness values gradually decrease with storage time, indicating that the microstructure produced by ECAP is inherently unstable and most probably some recovery/recrystallization occurs during the storage at room temperature. Figure 1b shows the true stress-true strain curves for the samples processed through 8 passes both immediately after ECAP and after 4 months in storage. For comparison, a stress–strain curve for the initial state is also plotted. In contrast to the initial state in the absence of ECAP, no strain hardening was observed after 8 passes of ECAP, thereby confirming the achievement of a saturation condition. For the sample pressed through 8 passes and stored for 4 months, there was a very significant reduction in the yield strength and a subsequent strain hardening, indicating that the change of microstructure evident in Fig. 1a is not due to a surface effect during storage at room temperature.

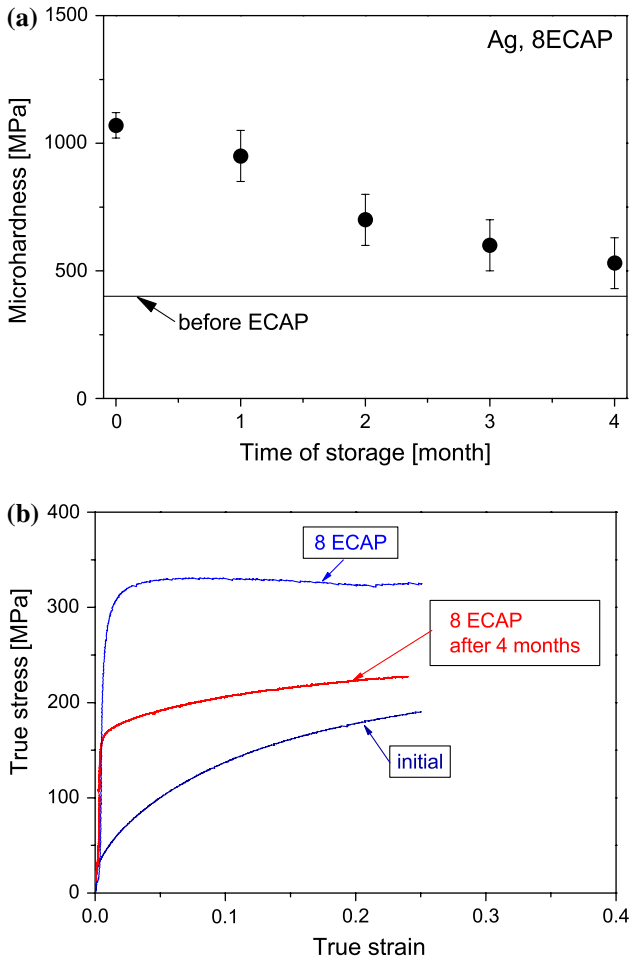

Fig. 1 Microhardness of Ag deformed by 8 ECAP passes as a function of storage time at room temperature (**a**). The horizontal line represents the hardness of the initial sample before ECAP. True stress-true strain curves obtained on silver samples before and after 8 passes and after storage at room temperature for 4 months (**b**)

As far as is known, this type of behavior was not previously reported for any material processed by ECAP. However, it should be noted that Schamp et al. [10] observed a relatively similar delayed softening in a wire-drawn copper. In these earlier experiments, a partial recovery/recrystallization of the microstructure was observed in the severely deformed surface region of a thin wire, 0.1 mm in diameter, which was strongly affected by the impurity concentration. It is important to note that the processing by severe plastic deformation in the present experiments was conducted on a pure material having dimensions which were larger than the thin wire by approximately two orders of magnitude.

The dislocation density was determined as a function of time using X-ray line profile analysis. The experimental results showed that after ECAP through 8 passes there was an average dislocation density of $\sim 46 \pm 5 \times 10^{14}$ m^{-2}, which is high by comparison with Au or Cu [7]. Figure 2a shows a Debye–Scherrer diffraction ring of the 220 reflection obtained after 8 passes of ECAP. It is seen that the intensity distribution along the ring is relatively homogeneous immediately after ECAP, thereby confirming there is a high degree of homogeneity within the microstructure. However, after 1 month, large intensity spots were visible on the Debye–Scherrer rings and these irregularities became more apparent with storage for 4 months. As an example, Fig. 2b shows the 220 reflection obtained from the sample processed by 8 passes and stored for 4 months. The high-intensity narrow peaks in the ring are scattered from grains where the dislocation density is low ($<10^{13}$–10^{14} m^{-2}) and the grain size is large (>1 μm), thereby indicating that in these volumes the microstructure has recovered/recrystallized strongly during storage at room temperature. The homogeneous parts of the Debye–Scherrer rings are related to the less recovered volumes where the average dislocation density is $\sim 15 \pm 2 \times 10^{14}$ m^{-2} as obtained from the analysis of X-ray line profiles.

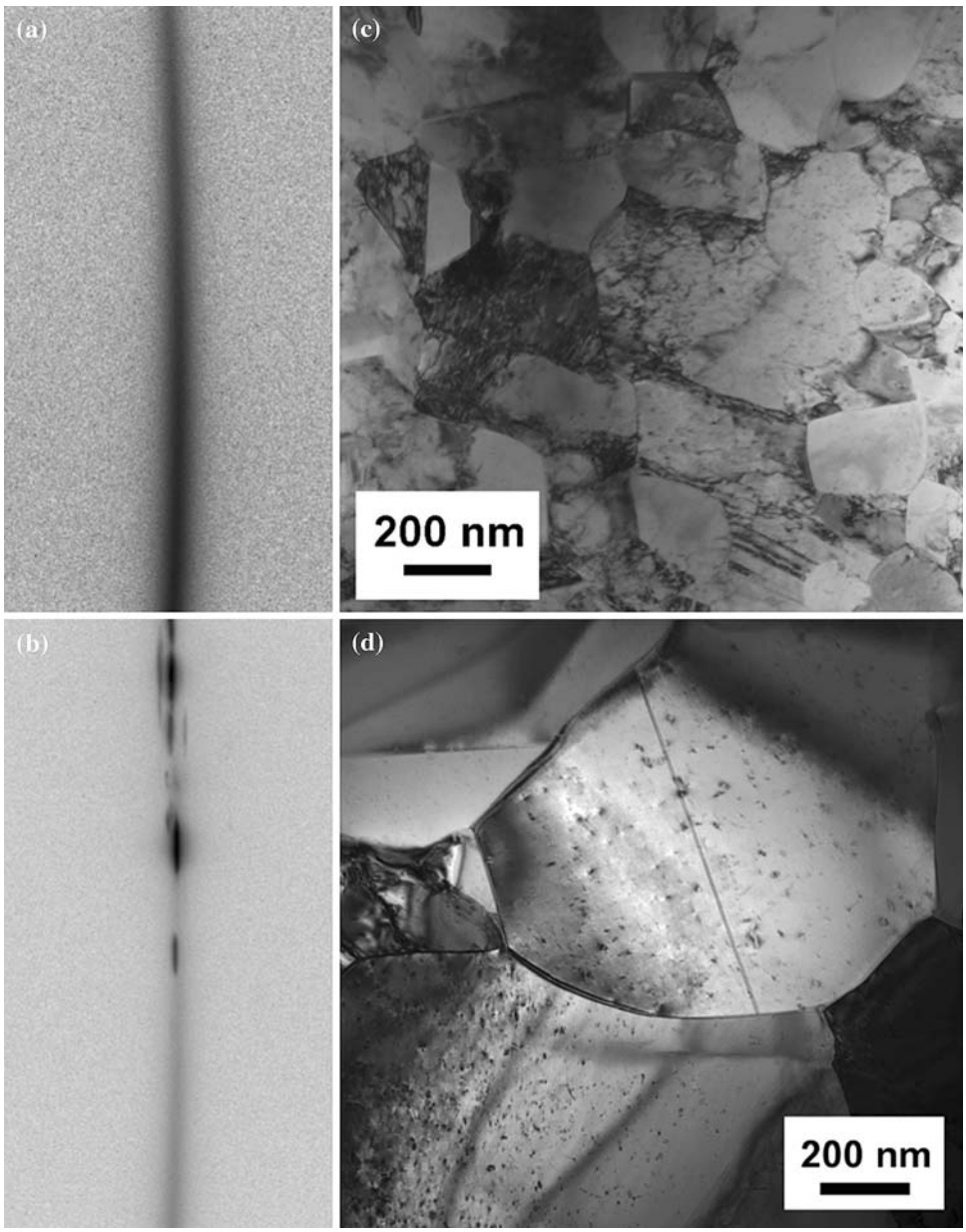

Fig. 2 Debye–Scherrer rings for the 220 reflection of X-rays and TEM images obtained on the microstructure of ECAP-processed Ag (**a**) and (**c**) immediately after 8 ECAP passes, as well as (**b**) and (**d**) after storage at room temperature for 4 months

Microstructural recovery is also apparent from a comparison of the two TEM images in Fig. 2c, d taken immediately following the 8 ECAP passes and after storage for 4 months, respectively. Inspection showed also that the grain size increased from $\sim$250 nm to $\sim$1 μm during storage for 4 months at room temperature.

The inhomogeneous intensity distributions in the Debye–Scherrer rings suggest that there is a fluctuation of the degree of recovery/recrystallization in the microstructure. The spatial distribution of the recovered volumes was monitored by making hardness map on the surface by nanoindentation. Figure 3 shows the nanohardness distributions in the initial material before ECAP, immediately after 8 passes of ECAP and after storage for 4 months. Thus, the hardness distribution changes significantly during storage at room temperature. Specifically, after 4 months of storage a fraction of the hardness distribution is shifted to lower values and some hardness values now coincide with those which were characteristic of the initial state.

The formation of an unstable microstructure in low stacking fault energy (SFE) ($\sim$16 mJ m^{-2} [11]) Ag is most probably due to the high degree of dislocation dissociation which initially impedes the cross-slip of dislocations during ECAP processing but this process may occur by thermal activation after sufficiently long times. In fcc metals the glide dislocations are dissociated into Shockley partials which border a ribbon of stacking fault. The equilibrium splitting distance (d) for dissociated screw

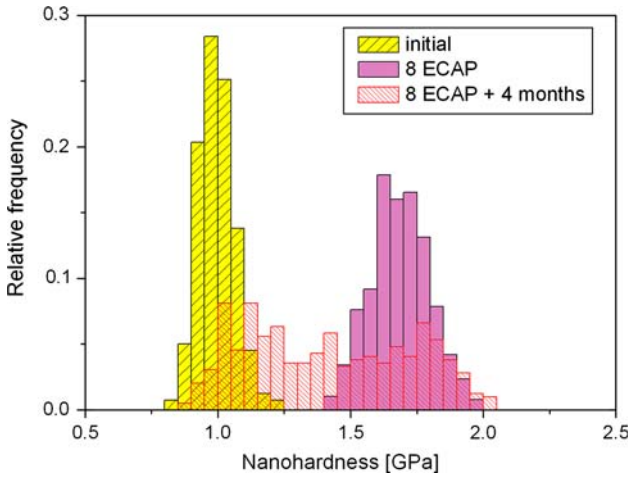

Fig. 3 Nanohardness distributions obtained in the initial state and in an ECAP-processed specimen immediately after 8 passes and after storage at room temperature for 4 months

dislocations may be conveniently defined in terms of the Burgers vector (b) by using the fractional term d/b. These fractions for pure Al, Ni, Cu and Au are 0.9, 3.1, 3.7 and 3.9 nm, respectively, where all of these values are much smaller than the equivalent value for Ag of 8.7 nm [12]. The cross-slip of screw dislocations is a thermally activated and stress-assisted process so that the probability of cross-slip decreases with increasing d/b [13, 14]. For example, in the absence of any assisting stresses, the waiting time for cross-slip in Ag may be calculated from the activation energy given by equation (17) by Escaig [14] and this is of the order of $\sim 10^{21}$ s, equivalent to $\sim 10^{13}$ years, which means in practice that cross-slip cannot occur in Ag. However, in the severely deformed microstructure there are significant internal stresses, originating primarily from the very high density of dislocations, and these stresses will assist the cross-slip process. Assuming, for example, a value for the assisting stresses in Ag of $G/3000$, the waiting time in silver is reduced to $\sim 10^{7}$ s. This means in practice that cross-slip may occur some months after the SPD processing, thereby giving a delayed recovery for the dislocation structures in Ag processed by ECAP in agreement with the present observations. Alternatively, taking pure Al, Ni, Cu and Au and again assuming $G/3000$ for the assisting stresses, the calculated waiting times are less than the duration of 8 ECAP passes ($\sim 10^{3}$ s). This means in practice that any cross-slip will occur during the ECAP processing which explains the absence of a delayed recovery for these materials. It is noted that the delayed recovery/recrystallization reported earlier in wire-drawn copper [10] is probably controlled by the impurity content of the sample because impurities usually reduce the stacking-fault energy of metals [15].

The inhomogeneous recovery of the dislocation structure is attributed to the stress-sensitivity of the probability of cross-slip [14]. In severely deformed polycrystals, the magnitude of the remaining stresses acting on the glide planes after deformation will change from grain to grain due to the distributions of the dislocations and other defects, such as twins, so that the driving force for cross-slip will depend upon the specific location within the specimen. As a result, it is anticipated there will be fluctuations in the waiting times for annihilation of dislocations and therefore the recovery starts inhomogeneously within the sample. It should be noted also that the grain growth observed in Fig. 2 indicates that, in addition to the recovery of the dislocation structure, recrystallization and/or grain boundary migration operate during the storage of the sample at room temperature. However, more detailed investigations are needed to reveal the contributions of these mechanisms.

In summary, the present results demonstrate a delayed recovery in severely deformed Ag which occurs a significantly long time after processing by ECAP. It is reasonable to assume this unusual microstructural instability occurs at a relatively low temperature due to the presence of highly dissociated dislocations. The large splitting distance between the partials impedes the cross-slip of dislocations during the ECAP procedure. At the same time, the internal stresses that are a consequence of the high density of dislocations lead to the annihilation of dislocations a relatively long time after processing. The present experimental results suggest that the reduced stability of the severely deformed microstructures in low SFE metals may affect the viability of these materials for use as structural components in long-term applications.

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